Sonderdruck aus: „Beiträge zur Tabakforschung" · Band 5 · Heft 2 · August 1969

3200

Temperature-Yield Profiles of Tobacco and Tobacco Constituents I

Borate-Treated and Untreated Tobacco*

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INTRODUCTION

As part of a continuing study (1) of the effects of chemical modifiers on the composition of cigarette smoke it has become desirable to elucidate the general mode of action of several of those additives which have caused a significant alteration of the levels of various smoke components.

Knowledge of the general mechanism of these modifiers will be valuable in the selection of future additives for screening. As a first step in the elucidation of the mode of action of a chemical modifier the temperature at which the action is operative must be determined. Comparison of the temperature-yield profiles for the pyrolysis of untreated and treated tobaccos will give this information. This paper describes the use of temperature-yield profiles to determine the temperature at which borate additives effect the pyrolysis of tobacco.

The pyrolysis procedure described here has been devised with the major emphasis on reproducibility. It would be difficult, if not impossible, to duplicate exactly the conditions under which the tobacco in a cigarette is burned. This work makes no attempt to do this. The intent is to pyrolyze treated and untreated tobacco under standard, reproducible conditions so as to be able to determine the temperature region in which various modifiers effect the yield of various smoke constituents.

EXPERIMENTAL

1. *Apparatus*

Figure 1 shows the apparatus used in this study. A vertically mounted 23 mm i.d. *Vycor* pyrolysis tube, D, is heated with a thermostated tube furnace. The tube furnace has a 30 cm heated zone, E. A layer of *Vycor* chips, F, are placed in the pyrolysis tube at the lower end of the heated zone. A "Y" shaped addition tube, A, is mounted on the top of the pyrolysis tube and the tobacco to be pyrolyzed is placed in the longer arm of this tube. The tobacco is added to the tube by advancing the plunger, B. A carrier gas is fed into the system through the gas inlet tube, C. The condensate is collected in a glass trap, G, which is filled with 1.5 mm glass helices and fully immersed in dry ice-acetone. A Cambridge filter, H, is affixed to the exit of the trap.

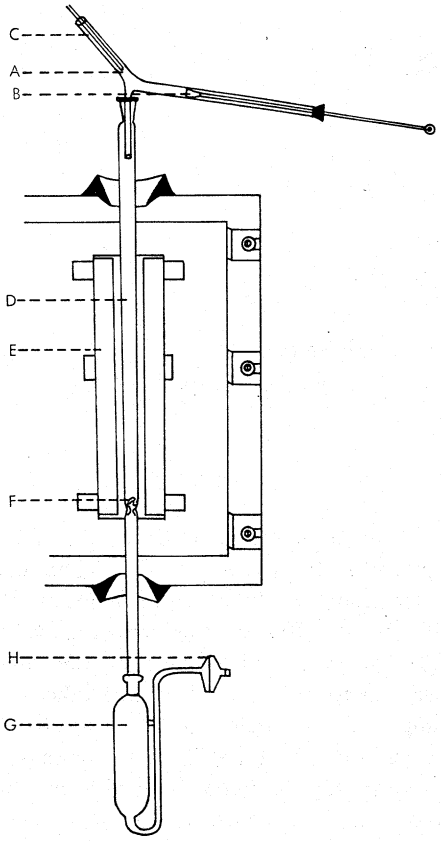
Figure 2a shows the actual temperature within the pyrolysis tube when the control is set at 600° C. It will be seen that this temperature is achieved only over a short length of the tube within the furnace. Being vertically mounted, the temperature rapidly decreases to near ambient at the lower portion of the tube. Figure 2b shows the temperature at the lower end of the heated zone of the furnace compared with the furnace temperature. This is the temperature at which the residue is held during the pyrolysis. No appreciable amount of secondary reaction should take place within the residue at these temperatures, although it is high enough to prevent condensation of product.

Tube pyrolysis is used in this work in an attempt to control the secondary reactions. Slow addition of tobacco through a preheated tube allows the tobacco to be uniformly pyrolyzed. Although bulk pyrolysis has been used in various pyrolysis studies, it has the disadvantage of the initial pyrolysis products being continuously exposed to the pyrolytic conditions throughout the entire reaction. This is especially undesirable when combustion modifiers are present which may catalyze secondary reactions not actually involved in the initial pyrolysis process. A second disadvantage of bulk pyrolysis is that as the sample is being heated to the desired temperature, pyrolytic reactions are taking place at lower temperatures. This is also true to some extent for tube pyrolysis. The tobacco particles are not immediately brought to the desired temperature, but the slow addition of finely divided

* Contribution from the Department of Agronomy, University of Kentucky, and the Eastern Utilization and Development Division, Agricultural Resarch Service, United Department of Agriculture. The investigation reported in this paper was carried out by cooperative agreement between the University of Kentucky Agricultural Experiment Station and the Eastern Utilization Resarch and Development Division and is published with the approval of the Directors of both the Experiment Station and the Eastern Utilization Resarch and Development Division. Presented, in part, at the 22nd Tobacco Chemists' Research Conference, Richmond, Virginia, October 17—19, 1968.

Figure 1 Pyrolysis apparatus

A, addition tube; B, plunger; C, gas inlet tube; D, Vycor pyrolysis tube; E, furnace; F, layer of Vycor chips; G, cold trap and H, Cambridge filter.



tobacco to a pyrolysis tube does eliminate the insulating effects of the entire tobacco mass that is present in bulk pyrolysis. In fact, the temperature differential in the type of pyrolysis done in this work will probably be more extreme toward elevated temperatures. Owing to the increased surface area which is exposed to the heated carrier gas ignition will take place more rapidly. This will be especially true in the cases of pyrolyses carried out in oxidizing atmospheres.

2. *Procedure*

Samples of the same tobaccos used for the manufacture of the experimental cigarettes (1) were dried, crushed, and sieved. The 20—30 mesh particles were used for all the pyrolyses described here. The moisture content of these samples was 7—9%. No attempt was made to increase the water content to 12% since difficulties were encountered in obtaining an even rate of delivery of the tobacco. A weighed sample of approximately 5 g of tobacco was placed in the long arm of the addition tube in front of the plunger. When gases other than air were used for the pyrolysis the assembled system was flushed with carrier gas for 10 min. prior to starting the pyrolysis. By slowly advancing the plunger the tobacco was gently tapped through the vertical section of the addition tube into the heated zone of the pyrolysis tube. The solid residue was caught on a layer of *Vycor* chips held in the pyrolysis tube at the lower portion of the heated zone of the furnace. The rate of addition was controlled so that a 5 g sample was added over a period of approximately 25 min. The flow rate for both air and nitrogen, which were employed as carrier gases in this work, was 30 ml/min. This gives a maximum dwell time of 4.2 min. for the gas in the heated portion of the pyrolysis tube. Release of volatile components will decrease the dwell time, especially at high temperatures.

The residue and *Vycor* chips were removed from the tube, separated and the residue weighed. The chips were returned to the tube which was washed with alternate 10 ml portions of 0.5 N sodium hydroxide solution and cyclohexane. The Cambridge filter was extracted with 3×3 ml of chloroform which was then also used to rinse out the pyrolysis tube. The condensate was recovered by washing the trap and helices with alternate portions of cyclohexane (approx. 5×30 ml) and sodium hydroxide solution (approx. 4×5 ml) and finally with 20 ml of chloroform. All of these solutions were combined and the condensate was partitioned into acidic, basic, and neutral fractions. The analysis of the phenols was performed as previously described (2). Owing to the interferences from the degradation products from nicotine in many of the pyrolyzates a procedure similar to that described by *Pyriki* (3) was used for the determination of recovered nicotine. In this method the forerun is steam distilled

Figure 2 a. Actual temperature within the pyrolysis tube with furnace set at 600° C. b. Temperature at which residue is held during pyrolyses.

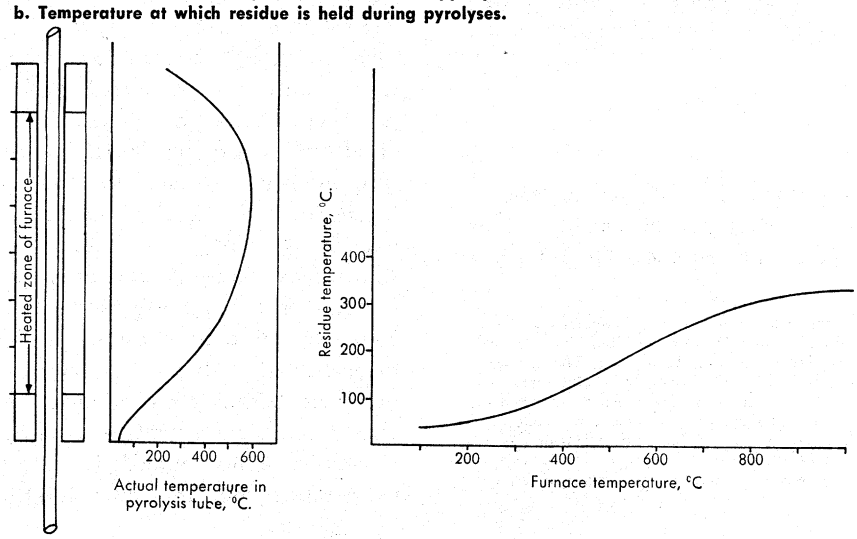


Table 1 Analytical Values for Untreated and Borate-Treated Cigarettes

	Per Cigarette	Per Gram of Tobacco Burned	Percent of TPM
Untreated			
TPM (mg)	36.84	52.90	100.0
Nicotine (mg)	2.46	3.53	6.14
Phenol (μg)	137	197	0.37
o-Cresol (μg)	24.6	35.3	0.07
m,p-Cresol (μg)	70.3	101	0.19
Benzo[a]pyrene (ng)	62.9	90.3	1.7×10^{-4}
Borate-Treated			
TPM	30.41	52.13	100.0
Nicotine	1.38	2.58	4.95
Phenol	263	492	0.94
o-Cresol	35.2	65.9	0.13
m,p-Cresol	113	212	0.41
Benzo[a]pyrene	120	224	4.3×10^{-4}

from an acetic acid solution instead of a hydrochloric acid solution. This removes pyridine and other monoacidic bases from the distilland prior to the steam distillation of the nicotine. Benzo(a)pyrene was determined by an isotopic dilution method (4).

In obtaining the temperature-yield profiles presented here, runs are first conducted at 100° C intervals from 200° C through 900° C or 1000° C. Pyrolyses with borate-treated tobaccos are not carried out at temperatures above 900° C because of the reaction of borate with *Vycor* at elevated temperatures. The maxima and minima which are indicated from the profile plotted with these 100° C points are confirmed by obtaining additional points. Smooth curves are then constructed over the points in order to illustrate the effect of the tobacco additives. Since only the relative shapes of these curves are being compared, any compression of maxima or minima is not felt to detract from their intended purposes.

RESULTS AND DISCUSSION

Borate-treated tobacco is of interest because of the substantial increase in the levels of phenols and benzo(a)pyrene found in the smoke of cigarettes made from these tobaccos. The flame-proofing action of borates has been recognized by the wood products industry for some time (5). The mixture of sodium tetraborate-boric acid in a 7:3 ratio is a well established (6) synergistic mixture for the flame-proofing of wood and textiles. It is this mixture that has been employed as the additive in this work. Borate salts, notably sodium tetraborate, do not markedly change the initial decomposition temperature, generally decrease the amount of tar formed and do not inhibit the glowing of cellulosic materials. It was because of these properties that this borate mixture was originally screened as a tobacco modifier. In choosing this additive a reduction of the TPM was expected, but the marked increase in the levels of phenols was not anticipated. Table 1 shows the analytical values for several components in the condensate obtained from cigarettes made from untreated tobacco and tobacco to which has been added 10% w/w of a 3:7 mixture of boric acid and sodium tetraborate decahydrate. The methods employed for the treatment of the tobacco and the manufacture and smoking of the cigarettes have been described in a previous publication (1). As seen in Table 1 the level of benzo(a)pyrene in the condensate of borate-treated cigarettes has been increased by a factor of 2.5. The various phenols have been increased from 1.9 for o-cresol to 2.5 for phenol. On a gram of tobacco burned basis, the TPM of the borate-treated cigarettes has not been significantly altered. Thus, contrary to our original expectations, the anticipated overall reduction of "tar" was not achieved, but there was a significant alteration of its composition.

It must be emphasized that borate-treated tobacco is not being suggested for use in smoking products. Investigation of this treated tobacco was undertaken to obtain information which may lead to the selection or development of tobacco additives of practical value. To ascertain the effects of an oxidizing and non-oxiziding atmosphere on the pyrolysis, untreated tobacco was pyrolyzed using both air and nitrogen as the carrier gas. There have been a number of studies reported in the literature involving the pyrolysis of tobacco (7, 8, 9), tobacco constituents (10), and tobacco additives (11). Based on the investigation of *Newsome* and *Keith* (12), which shows the presence of a reducing atmosphere behind the burning cone of a cigarette, it seems reasonable to conduct pyrolyses in inert atmospheres. *Wynder* and *Hoffmann* (13) adequately justified pyrolysis in nitrogen atmospheres for the collection of condensates for biological investigations. However, for the study of combustion modifiers it is felt that pyrolyses in an oxidizing atmosphere will be more meaningful. Thermal analytical studies have shown (14) that there is a greater difference between treated and untreated

Figure 3 Temperature-yield profile for nicotine.
Untreated tobacco in air . . . . . , untreated tobacco in nitrogen ---------- and borate-treated tobacco in air ———.

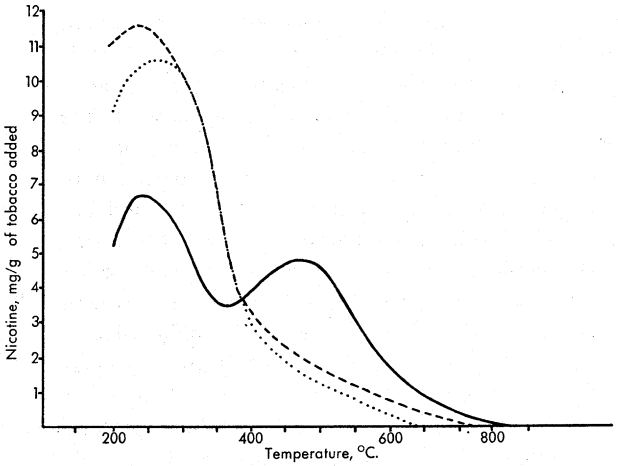


Figure 4 Temperature-yield profile for benzo(a)pyrene.
Untreated tobacco in air . . . . . , untreated tobacco in nitrogen ---------- and borate-treated tobacco in air ———.

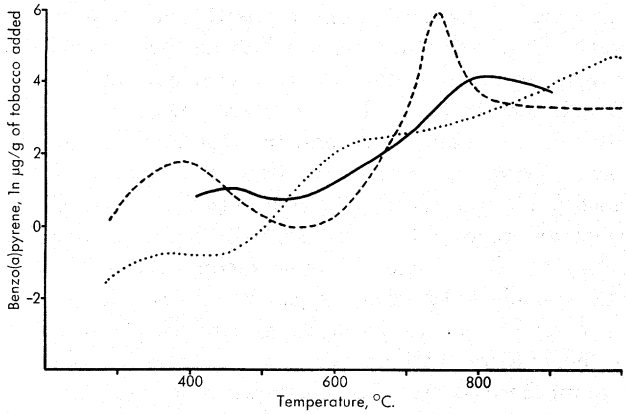


Figure 5 Temperature-yield profile for o-cresol.
Untreated tobacco in air . . . . . , untreated tobacco in nitrogen ---------- and borate-treated tobacco in air ———.

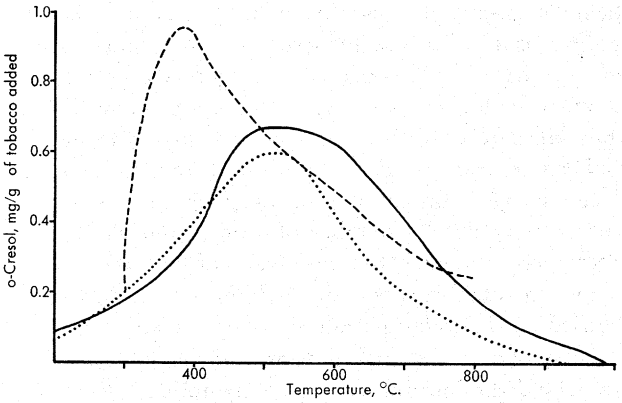


Figure 6 Temperature-yield profile for m,p-cresol.
Untreated tobacco in air . . . . . , untreated tobacco in nitrogen ---------- and borate-treated tobacco in air ———.

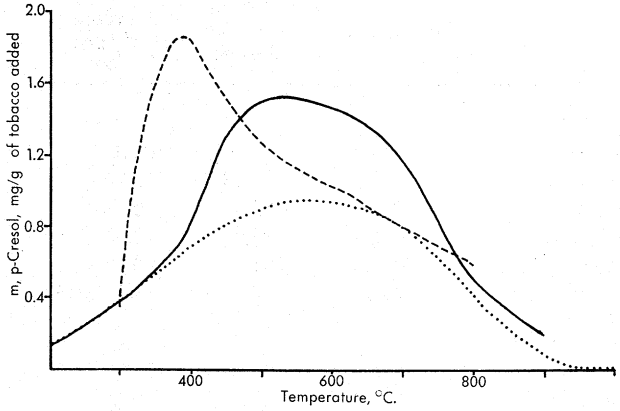
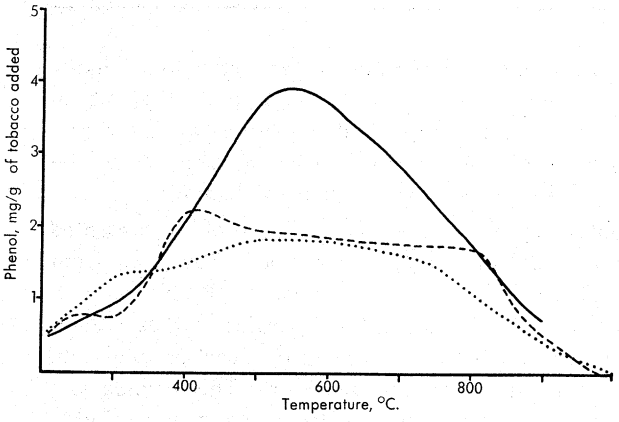


Figure 7 Temperature-yield profile of phenol.
Untreated tobacco in air . . . . . , untreated tobacco in nitrogen ---------- and borate-treated tobacco in air ———



tobaccos in an oxidizing atmosphere than in an inert atmosphere. However, since much pyrolytic work with tobacco has been carried out in a nitrogen atmosphere, we have included the temperature-yield profiles obtained for untreated tobacco in nitrogen for comparison. Figures 3–5 show the temperature-yield profiles for several compounds in the condensate obtained from the pyrolysis of untreated and borate-treated tobaccos.

1. Nicotine

In both air and nitrogen the temperature of maximum recovery of nicotine is approximately 250° C. This is to be expected since the boiling point of nicotine is 247° C. This is followed by a rapid decrease in the recovery of nicotine at temperatures above 300° C. The similarity of the profiles in air and nitrogen may seem to conflict with the findings of *Kobashi* and coworkers (15). These investigators found that nicotine is almost completely degraded in an atmosphere of air by 350° C, whereas it remains unchanged in nitrogen up to 600° C. It is to be expected that burning tobacco would not give an "inert" environment for the pyrolysis of nicotine in nitrogen. Thus, the mode of pyrolysis of nicotine in tobacco should be similar in both air and nitrogen. While it is true that a great deal of valuable information can be obtained from the pyrolysis of pure tobacco constituents, the results must be regarded only as indicative of what takes place within the burning tobacco matrix. It must be pointed out in the case of these curves for nicotine that the yield represents only the recovery of a leaf constituent. No pyrolytic formation is involved. This is unlike the subsequent curves for the phenols and benzo(a)pyrene where pyrolytic formation is involved. An interesting aspect of the profile for nicotine recovery from borate-treated tobacco is the presence of the second peak at approximately 450° C. This second maximum is probably due to the relatively slow release of nicotine from a borate salt or complex. This released nicotine would have a shorter dwell-time in the heated zone of the tube, thus allowing more undegraded nicotine to be collected. Another, and less probable, explanation for this second maximum is that the sodium tetraborate-boric acid mixture has coated the tobacco particles to form a physical barrier which inhibits the release of the nicotine. DTA studies with the 3:7 boric acid-sodium tetraborate decahydrate mixture have shown that a first melting point occurs at 86° C. Thus, at the temperatures in question the additive is a liquid and this liquid phase should not form an effective barrier to the release of nicotine. A partial covering of the tobacco

with either a solid or a liquid surface coating might be expected to extend the first peak, but not to give two distinct maxima as is observed. This secondary release of nicotine may be unique to this particular technique of pyrolysis and is probably not an important process in the burning cigarette.

2. Benzo(a)pyrene

The temperature-yield profile for benzo(a)pyrene is shown in Figure 4. In order to compress the ordinate the benzo(a)pyrene values are plotted as the natural logarithms of the recoveries. Untreated tobacco in air shows no maximum in the temperature-yield profile. This closely parallels the findings of previously published results. *Grimmer* (9) found a nearly linear correlation between pyrolysis temperature and the logarithm of benzo(a)pyrene recovery. Because of the high flow rates (1000 and 1500 ml/min.) employed by these workers a value closer to the true "formation" of benzo(a)-pyrene is obtained. The much lower flow rate (30 ml/min.) used in this work allows for considerably more destruction of the benzo(a)pyrene formed, especially at higher temperatures.

The maxima and minima shown between 300° C and 500° C have been confirmed and are, indeed, real. The possibility of this being background caused by the sublimation of benzo(a)pyrene present on the leaf is not possible. Presence of benzo(a)pyrene on tobacco leaf has been reported by several groups (16,17) to be in the order of 12—20 ppb. *Lyons* (18) und *Bentley* and *Burgan* (19) have shown that the benzo(a)pyrene present in the leaf did not appreciably contribute to benzo(a)pyrene present in the smoke. Analysis of the tobacco used in these pyrolyses showed the presence of 13 ppb of benzo(a)pyrene on the leaf. This would give a background of −4.3 on the logarithmic scale of the profiles shown.

DTA studies (14) with tobacco have shown that exothermic reactions start at approximately 220° C in an inert atmosphere. Thus, it is conceivable that there is some benzo(a)pyrene being formed during pyrolyses conducted with furnace temperatures below 400° C owing to the increase in the temperature of the tobacco itself. For pyrolysis temperatures around 400° C the benzo(a)pyrene will be released into an environment below the temperature at which the rate of destruction of benzo(a)pyrene is significant. At slightly higher pyrolysis temperatures, there will be little increase in the rate of benzo(a)pyrene formation, but because of the increase in the rate of destruction a minimum will be generated in the profile. Thus, the minima in these profiles do not necessarily result from a decrease in the formation of a particular pyrolytic component but may be due to a disproportionate increase in the rate of destruction of a component as compared with its pyrosynthesis. These secondary reactions will be more pronounced when low flow rates of carrier gas are employed and become excessive during bulk pyrolysis when no carrier gas is employed to remove the products as they are formed.

In nitrogen a maximum in the benzo(a)pyrene recovery occurs at 740° C. This is in reasonable agreement with the maximum found by *Badger* (20) for the formation of benzo(a)pyrene from n-butylbenzene in an atmosphere of nitrogen. These workers found the optimum temperature for benzo(a)pyrene formation to be 710° C. This was a gas phase addition of a pure precursor to a silica tube, packed with porcelain chips. Flow rates or dwell times were not reported for the system used.
At temperatures below 530° C there is more benzo(a)-pyrene recovered from the borate-treated tobacco than from the untreated tobacco. From 530° C to 710° C there is less benzo(a)pyrene recovered from the borate-treated tobacco. At pyrolysis temperatures above 710° C the borate-treated tobacco leads to a higher benzo(a)-pyrene recovery with a maximum slightly above 800° C. The relative shapes of the profiles above 500° C are suggestive of a precursor for benzo(a)pyrene being complexed by the borate.

3. o-Cresol

In the case of o-cresol there are major differences seen in the temperature-yield profiles for untreated tobacco being pyrolyzed in air and in nitrogen. Two rationalizations may be offered for this. There may be different mechanisms involved for the formation of o-cresol in air and in nitrogen, or the rate of destruction of o-cresol in the pyrolyzing tobacco is greatly accelerated in air at temperatures between 300° C and 500° C, or a combination of these may be involved. A comparison of the profiles for untreated and borate-treated tobaccos indicates that there is no major change in the mode of formation of o-cresol. Both the untreated and borate-treated tobacco show a broad maximum at approximately 500° C. The almost two-fold increase in the level of o-cresol found in the condensate from borate-treated cigarettes is reflected in the higher temperature regions of the profiles.

4. m-, p-Cresol

The same type of profiles are shown for the recovery of the mixture of m- and p-cresols as has been discussed for o-cresol. Again, no apparent change in the mode of formation of m-, p-cresol has been brought about by the addition of borate to the tobacco.

5. Phenol

In both air and nitrogen two maxima for the recovery of phenol are apparent. Both maxima are shifted to higher temperatures for the pyrolysis in air. We believe that this represents two distinct modes of phenol formation. This first maximum shown in the profiles for the untreated tobacco is not due to the distillation of phenol present in the leaf into the condensate. Analysis of the free phenol present in the leaf gave a value of 43 µg/g. This would give a background phenol level of 0.043 on the ordinate of the temperature-yield profiles as shown here. Comparing the profiles for the pyrolysis of untreated and borate-treated tobaccos in air, it is seen that the first region of phenol formation is

virtually eliminated, whereas the second region is greatly increased. This is similar to the situation shown by the thermogravimetric studies which have been performed with borate-treated tobaccos (14). The TGA curve for borate-treated tobacco shows a decrease in the weight loss in the low temperature region and an increase in the weight loss in the high temperature region when compared with that of untreated tobacco. The effect of borate on the pyrolysis of cellulose and of lignin will be presented in a forthcoming paper. In this report it will be shown that the addition of borate to lignin decreases the phenol recovery at lower temperatures. Also, that the addition of borate to cellulose greatly increases the recovery of phenol at higher temperatures.

SUMMARY

Analyses of the smoke from cigarettes made from borate-treated tobacco have shown a significant increase in the levels of phenol, o-cresol, m-, p-cresol, and benzo(a)pyrene. To determine the temperature range at which this additive is operative temperature-yield profiles from tube pyrolyses have been obtained for both untreated and borate-treated tobacco. The profile for untreated tobacco indicates that there are two distinct modes of phenol formation. Addition of borate to the tobacco suppresses phenol formation at lower temperatures and greatly enhances its formation at higher temperatures. The modes of formation of the cresols do not appear to be markedly altered by the addition of borate to tobacco.

ZUSAMMENFASSUNG

Analysen des Rauches von Cigaretten, deren Tabak Borat zugesetzt worden war, zeigten einen deutlichen Anstieg der Phenol-, der o-, m- und p-Kresol- sowie der Benzo-a-pyren-Konzentration. Um zu bestimmen, innerhalb welcher Temperaturzone das Additiv wirksam ist wurden Temperatur-Ausbeute-Kurven mittels Rohrpyrolyse von unbehandeltem und borathaltigem Tabak aufgenommen. Für den unbehandelten Tabak zeigt die Kurve zwei unterschiedliche Mechanismen der Phenol-Bildung. Borat-Zusatz unterdrückt die Phenol-Bildung bei niedrigen Temperaturen und begünstigt sie in starkem Maße bei höheren Temperaturen. Die Bildungsweisen der Kresole scheinen durch Zusatz von Borat zum Tabak nicht wesentlich beeinflußt zu werden.

RÉSUMÉ

L'analyse de la fumée de cigarettes en tabac traité par un borate a mis en évidence un accroissement significatif des taux de phénol, *o*-crésol, *m*-, *p*-crésol et benzo(a)pyrène. Pour déterminer l'intervalle de température dans lequel cet additif agit, on a établi au moyen de pyrolyses en tube, les profils température-rendement des tabacs traités, ou non-traités, par le borate. Le profil du tabac non-traité indique qu'il existe deux modes distincts de formation des phénols. L'addition de borate au tabac supprime la formation du phénol aux températures inférieures et l'accroit fortement aux températures supérieures. Les modes de formation des crésols ne semblent pas nettement modifiés par l'addition de borate au tabac.

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